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PROCEEDINGS
OF THE
NATIONAL ACADEMY OF SCIENCES
Volume 1 DECEMBER 15, 1915 Number 12

SALTS, SOIL-COLLOIDS, AND SOILS

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Presented to the Academy, November 1, 1915

To reclaim permanently and manage alkali lands successfully, or to use fertilizer salts with intelligence and profit, requires a consideration of the effects of these salts on the physical condition of soils. Not only must we bear in mind the effects of the salts while present in the soil, but also the condition that may result when these same salts are removed partially or wholly by natural or artificial drainage. In our experience in California this latter phase has proved to be a more difficult and perplexing problem than the former. The importance of this subject justifies the publication of this brief discussion, prior to the appearance of the detailed statement with reference to three years of work which we have carried out upon it.

We know that, if a salt is added to a soil suspension, certain obvious effects are produced. Thus the common acids and their salts with the alkalies, the alkaline earths, and the heavy metals, as well as many other salts, flocculate suspensions in water of the soil mass. We associate this flocculated condition with an improvement in the working qualities of the soil. Another class of salts, those which give rise to an alkaline reaction, such as the alkaline hydrates, and as assumed, the alkali carbonates, possess within certain concentrations, the opposite power of deflocculating soil suspensions. Field soils so affected reflect this condition by their imperviousness to water and their inferior cultivating qualities.

Undoubtedly these phenomena are to be associated with the soil particles of such a fine state of division as to make their relatively large surface a factor of special importance. Possibly such particles may properly be designated colloids. Hence in attempting to explain salt effects on soils, we must look to the laws formulated from studies on colloidal materials. Foremost among these may be mentioned those concerning the migration and electrical charges of colloids by Picton and Linde[1] and the subsequent contribution by Hardy,[2] setting forth the important rule that ions which carry charges opposite to those associated with particular colloids will act as precipitants for those colloids. This rule could be anticipated from the previous discovery of Schulze[3] that the flocculating power of an ion is in some measure dependent upon its valence. More recently Tolman[4] has gone over the field anew, and, by assuming that stable colloidal solutions exist only when the surface tension between the particles and the liquid is equal to zero, has developed a very interesting and highly plausible theoretical explanation for the phenomena occurring in dispersoid systems. By means of these facts we are able to predict with some assurance the effect accompanying the constant presence of a particular salt on the physical condition of a soil. It is of particular significance in this connection to remember, however, that these conceptions regarding the behavior of colloids are based on systems wherein the salt remains in contact with the particles. Such is rarely the case in normal field soils; for various agencies are constantly affecting the position of the salts, and as we shall see the leaching out of certain salts from a soil seems to produce an entirely new system, to which the laws referred to may not be strictly applicable. At least the conditions are sufficiently puzzling to merit the following discussion.

If a soil to which sodium chloride or sulphate has been added is subjected to leaching processes, it assumes an entirely new set of physical properties, characterized by a more or less complete deflocculation.[5] Evidently a new system, differing from that composed of the soil in contact with its own solution, or in contact with the salt solution, has resulted from the treatment. This phenomenon was first observed by us in a field experiment consisting of cylinders containing a clay loam soil at Davis, Cal., to which solutions of sodium chloride, sulphate, and carbonate had been added. It will suffice here to say that the salt-treated soils became very impervious to water during the winter season, and when dry were extremely intractable. The untreated control soils were easily managed at all times.

Results similar to those observed in the field were secured in the laboratory when sodium lactate, acetate, nitrate, chloride, sulphate, carbonate, and hydrate, potassium chloride, and sulphate, and ammonium sulphate were washed from the Davis soil. Magnesium chloride is also slightly effective in the same direction, while calcium chloride and barium chloride, when similarly leached from it, seem to leave the soil in its original condition. Not only were various salts tried, but also various soils with the same salt. Thus the washing out of sodium chloride from the Davis clay loam, the Berkeley adobe, the Anaheim sandy and the Oakley blow sand brought about a marked increase in the diffusion of the soil colloids. Apparently, then, we are dealing with a phenomenon of general application.

Turning to the literature we find reports of some interesting observations which concern the phenomenon under consideration, Adolph Mayer[6] noted a decrease in percolation when certain salts are washed from soil; and according to Van Bemmelen[7] the same thing occurs when clays or the hydrated oxides of tin, silica, and manganese are treated in the same manner. He also calls attention to the turbidity of the filtrate which appears as the salts are washed out. A similar turbidity has been observed by us in the filtrates from soils being washed free of salts. Warington[8] also refers in a general way to the appearance of somewhat similar phenomena when soils previously treated with acids are washed with water. Some further observations pertaining to this subject have also been recorded by Warington,[9] Hall,[10] Krüger,[11] McGeorge,[12] and others. Their observations dealt in the main with fertilizer salts and particularly with the after effects of sodium nitrate. In general, the ill effects of long continued use of this salt, are attributed to the formation of sodium carbonate.

Finding that the salt and water treatment of soils referred to brought about such striking results, some experiments were undertaken with the view of studying the mechanism by which these effects are produced. These investigations followed certain theories which had been advanced to account for the soil conditions noted above.

If a soil which has been treated as outlined above is suspended in water it yields a suspension much richer in solid matter than a suspension similarly formed from the untreated soil. Boiling the normal soil in distilled water produces a somewhat similar effect. Likewise, the same general condition of diffusion appears if NaOH in certain concentrations is added to a suspension of the normal soil. We also found that it required more NaCl to flocculate the suspension of a soil from which this salt had been previously leached than to flocculate a suspension of the normal soil. Evidently the colloids of the salt-treated soil are in a high state of diffusion. Furthermore, there is some indication that colloids of a new type, or perhaps additional colloids of the same general type, have been formed.

In either case an increase in the internal surface of the soil would be expected. That such an increase had occurred seemed evident from the data secured by the use of Briggs'[13] centrifugal method for moisture-equivalents. However, a study of the hygroscopic coefficients of the variously treated soils failed to reveal any increase in surface. In all probability Mitscherlich's[14] method would be the most appropriate one for obtaining information regarding this point, but it has not yet been tried by us.

The interchange of ions when salt solutions are placed in contact with soils forms the working basis for the hypothesis that new colloids have been formed. The filtrates from soils which have received salt applications followed by leaching with water contain calcium and magnesium in amounts chemically equivalent[15] to the sodium taken up in exchange therefor by the silicates. It is to this new sodium silicate compound as the first possibility that we attribute the increased colloidal properties noted above. Potassium and ammonium salts seem to produce similar compounds, while calcium and barium salts under the same conditions do not produce the colloidal hydrated silicates. These new substances, together with the normal soil colloids, remain in a flocculated condition as long as free acid[16] or an excess of the soluble salts added or those formed by the interchange is present.

As flocculated colloids their effect on the physical condition of the soil is either beneficial or passes unobserved. Hence as long as salts are present in sufficient quantity no objectionable feature appears, but when these flocculating agents are removed by leaching with water, the colloids become diffused and offer great resistance to the further passage of water.

In explanation thereof, we might assume in accordance with Tolman's ideas that the normal lyophobic soil colloids when suspended in water have a positive surface-tension, hence greater than zero, but that the new hydrated sodium silicate when suspended in the same medium automatically provides by hydrolysis a sufficient quantity of OH ions to lower this surface-tension and to bring it nearer the zero value, so that the colloids, in this case, would have a far greater tendency to become and to remain dispersed. This assumption requires the consideration that both the normal colloids and those resulting from the interchange of ions carry negative charges, which brings us immediately to our next hypothesis which deals in the main, with the nature of the suspending medium, rather than with the changes occurring in the solid substances.

This hypothesis is largely based on the contention that the behavior of soils under the influence of salts agrees in some measure with the laws which are thought to govern the behavior of dispersed systems to which salts have been added. Obviously this would be the case when we are considering suspensions of the soil mass in various solutions. Some doubt, however, may be expressed as to the validity of this statement when a soil of normal moisture content is compared to the dispersoid of a disperse system, or to a soil suspended in a liquid. For in the normal soil such factors as the surface tension of the liquid-air surface may be of such magnitudes as to materially alter conditions so that the laws referred to would not be applicable to such systems. In order to see how far the analogy can be drawn let us consider, for example, clay. Clay has been shown to be a lyophobic colloid which assumes the negative charge of OH ions when suspended in water. The addition of more OH ions as by NaOH within certain limitations lowers the solid-liquid surface-tension so that a greater diffusion results. If a positive ion is added to the system, the OH ions are neutralized, the surface-tension increases, and the clay particles increase in size until they finally settle to the bottom of the vessel. So far the well known facts agree with the theory and, moreover, it is evident that the nature of the medium of suspension is an important factor. When a salt, such as sodium chloride, is added to a soil and subsequently leached out, it may be possible that the medium of suspension has been materially altered. The selective adsorption of the sodium by the soil may eventually give rise to OH ions, in which case the soil would become more or less diffused. By means of the hydrogen electrode we have been able to obtain specific data with respect to the quantity of OH ions present in the medium of suspension. Our results so far indicate that there is not a sufficient quantity of OH ions in the solution bathing the soil particles of the salt treated soil, to account for its unusual degree of diffusion. These data bear significantly on the general behavior of the soil suspension under various conditions.

If a soil which has been previously treated with salt and leached with water is subjected to drying at 130° C., it loses only a small portion of its diffusible colloidal material. Whatever other bearing this may have upon the subject, it at least indicates that the change is of a permanent character.

In the course of these investigations we have also noted that salt solutions of low concentration (less than $\frac{1}{1500}$ normal) have little or no effect on a soil suspension, so that the mere dilution of the salt solutions can not account for the effects observed. Moreover, it has been found that it is not necessary to wash the soil entirely free from salt in order to produce the deflocculated condition.

One other interesting observation with respect to the difference in behavior of sodium hydroxide and carbonate came to our notice. Sodium hydrate is a stabilizing agent in a fairly wide range of concentrations. Sodium carbonate, on the other hand, failed to stabilize at any concentration. Both substances are precipitating agents at concentrations greater than $\frac{1}{15}$ normal. Our studies with the hydrogen electrode include systems of soil suspended in various concentrations of these substances. In case sodium hydroxide or carbonate is added to a soil the bases combine directly with the silicates forming addition-compounds, as has been also pointed out by Sullivan (loc. cit.[15]). Water or carbonic acid is the end-product, hence the washing process so essential for the appearance of diffusion in soils after the use of neutral salts is not so necessary in the case of alkaline salts.

Briefly stated the experiments upon which the above summary is based have enabled us to throw upon the subject of salts in relation with soil colloids a light which has never before, particularly by soil chemists, been cast upon it. Not only is the way opened for an extensive experimental field in the physical chemistry of the soil, but there are indications that the principles involved, part of which are for the first time gathered together and correlated by us, will be of profound practical significance in the important subjects both of 'alkali' and of fertilizer salt applications to soils. Many of the perplexing aspects of the physical effects of continued nitrate of soda and other fertilizer applications to soils, as well as those following the leaching out of alkali, will, we hope, be largely cleared up by the investigations soon to be reported at length.

My thanks are due to Dr. Chas. B. Lipman for many helpful suggestions and for his critical reading of the manuscript.

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[1] *London, J. Chem. Soc.*, **71**, 568 (1897).

[2] *London, Proc. R. Soc.*, **66**, 115 (1899).

[3] *J. prakt. Chem., Leipzig*, Ser. 2, **25**, 445 (1882).

[4] *J. Amer. Chem. Soc.*, **35**, No. 4 (1913).

[5] Free has already discussed flocculation as a matter of degree—*Philadelphia, J. Frank. Inst.*, 1910.

[6] *Forsch. auf dem Gebiete der Agrik. Physik*, Vol. 2, 1879, p. 251.

[7] *J. prakt. Chem.*, Ser. 2, **23**, 388 (1881).

[8] *Physical Properties of Soil*, Cambridge Univ. Press, 1900, p. 30.

[9] Loc. cit.

[10] *The Soil*, 1910, p. 252; also *London, J. Chem. Soc.*, **85**, 964 (1904).

[11] Cited from *U. S. Dept. Agric. Off. Exp. Sta. Rec.*, **29**, No. 8, 719 (1908).

[12] *Hawaiian Agric. Exp. Sta., Bull.* No. 35, 1914.

[13] *U. S. Dept. Agric. Bur. Soils, Bull.* No. 45.

[14] *Bodenkunde für Land-und Forstwirte*, p. 51.

[15] After reviewing this subject Sullivan draws the following conclusion—"So far as the evidence goes, then, the action of silicates, clay, and other constituents of the earth's crust on solutions of such salts as do not dissolve in water with alkaline reaction consists in an equivalent exchange of bases." *U. S. Geol. Sur., Bull.* No. 312, p. 27 (1907).

[16] For a discussion of the presence of free acid in salt solutions in contact with soils the reader is referred to the work of Parker, *J. Agric. Res.*, **1**, 179 (1913).